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(54) PRODUCING METHOD FOR FINE PARTICLE FOR FORMING INSOLATION SHIELDING FILM AND APPLICATION LIQUID FOR FORMING INSOLATION SHIELDING FILM USING THE FINE PARTICLE OBTAINED BY THE PRODUCING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a producing method for a fine particle for forming an insolation shielding film which produces fine particles for forming the insolation shielding film which is capable of forming insolation shielding film of which the insolation transmittance at visible light transmittance of $\geq 80\%$ is less than 70% and the haze value is less than 1% in a shorter time than the conventional method.

SOLUTION: This producing method of the fine particle for forming an insolation shielding film is characterized in that indium tin oxide fine particles the averaged grain size of which is < 100 nm and tungsten oxide fine particles or rhenium oxide fine particles are mixed and are heated and treated under an atmosphere of inactive gas including alcohol or an atmosphere of mixed gas of a reducing gas and an inactive gas and the fine particles for forming insolation shielding film can be produced in a shorter time than the conventional method thanks to the catalytic action of the tungsten oxide fine particles or rhenium oxide fine particles which are added to tin- containing indium oxide fine particles at the time of heat treatment.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the particle for solar radiation screen formation characterized by heat-treating under the inert gas ambient atmosphere in which a mean diameter mixes an indium stannic acid ghost particle, a tungstic-acid ghost particle, or a rhenium oxide particle 100nm or less, and contains alcohol in the manufacture approach of the particle for solar radiation screen formation, or the mixed-gas ambient atmosphere of reducibility gas and inert gas.

[Claim 2] The manufacture approach of the particle for solar-radiation screen formation characterized by to heat-treat under the inert-gas ambient atmosphere in which the amount of residual impurities which consists of the chlorine ion which mean particle diameter is 100nm or less, and is contained in a particle in the manufacture approach of the particle for solar-radiation screen formation, nitrate ion, and sulfate ion mixes the indium stannic-acid ghost particle, the tungstic-acid ghost particle, or the rhenium oxide particle which is 0.6 or less % of the weight, and contains inert gas or alcohol, or the mixed-gas ambient atmosphere of reducibility gas and inert gas.

[Claim 3] The manufacture approach of the particle for solar radiation screen formation according to claim 1 or 2 that the mixed rate of the above-mentioned indium stannic acid ghost particle and a tungstic-acid ghost particle is characterized by being 99.9:0.1-80:20 in a weight ratio.

[Claim 4] The manufacture approach of the particle for solar radiation screen formation according to claim 1 or 2 that the mixed rate of the above-mentioned indium stannic acid ghost particle and a rhenium oxide particle is characterized by being 99.9:0.1-99:1 in a weight ratio.

[Claim 5] Coating liquid for solar radiation screen formation characterized by containing the particle for solar radiation screen formation according to claim 1 to 4, a solvent, and a binder.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention Aperture material, such as a car, a building, an office, and a general residence, a telephone booth, The particle for solar radiation screen formation applied to glass, such as a show window, a lamp for lighting, and a transparence case, and the transparence base material which needs the solar radiation electric shielding function of plastics and others is started. Especially, moreover, the solar radiation permeability at the time of 80% or more of light permeability is related with the coating liquid for solar radiation screen formation using the particle obtained by the manufacture approach of the particle for solar radiation screen formation which can form the solar radiation screen whose Hayes value is less than 1%, and this manufacture approach at less than 70%.

[0002]

[Description of the Prior Art] The approach of forming the ingredient which reflects the wavelength of visible and an infrared region in a glass front face, and using as heat reflective glass is conventionally performed by making a heat component into the approach of removing and decreasing from the external light sources, such as sunlight and an electric bulb. And as the above-mentioned ingredient, metallic oxides, such as FeOx, CoOx, CrOx, and TiOx, and the metallic material which has free electrons, such as Ag, Au, Cu, nickel, and aluminum, so much have been chosen.

[0003] However, since the light also had the property reflected or absorbed in coincidence in addition to the near infrared ray greatly contributed to a thermal effect, there was a problem to which light permeability falls in these ingredients. And in the transparence base material used for building materials, a vehicle, a telephone booth, etc., since the high permeability of a light field is needed, when using said ingredient, thickness must be made very thin. Therefore, being formed membranes and used for the thin film of 10nm level using the physical forming-membranes methods, such as spray printing, a CVD method, or a spatter, vacuum evaporation technique, is usually performed. And these membrane formation approaches needed large-scale equipment and a vacuum facility, and since a problem was in productivity or large area-ization, they had the fault that a membranous manufacturing cost was high.

[0004] Moreover, when thickness tended to be made thin using the above-mentioned forming-membranes method and it was going to make the permeability of the light high, the membranous solar radiation electric shielding property fell, thickness was thickened on the contrary, and when the solar radiation electric shielding property was made high, there was also a problem to which the film becomes dark.

[0005] Moreover, when it was going to make the solar radiation electric shielding property high with these ingredients, the reflection factor of a light field also tends to become coincidence high, and the trouble which gives an appearance [GIRAGIRA / appearance] like a mirror and spoils a fine sight also existed.

[0006] Furthermore, there are many to which membranous conductivity becomes high with these ingredients. And when membranous conductivity was high, the electric wave of a cellular phone, TV, radio, etc., etc. was reflected, it became non-receipt and there were also problems, such as causing an electromagnetic interference in a circumference area.

[0007] On the other hand, the resin film which added organic system near infrared ray absorbents, such as a phthalocyanine system metallurgy group complex system, in the binder is also used. However, compared with the ingredient of an inorganic system, degradation by heat or humidity is remarkable, and weatherability had a fault.

[0008] In order to improve the fault of such a conventional solar radiation screen, the reflection factor of the light of a light field was low as a membranous physical property, permeability was high, and while the permeability of an infrared field was low, it was required for membranous conductivity to be able to form the more controllable film in general than [106ohms /] **.

[0009]

[Problem(s) to be Solved by the Invention] By the way, as an ingredient in which light transmission moreover has a solar radiation electric shielding function highly, antimony content tin oxide (ATO) and tin content indium oxide (ITO) are also known, and the appearance [GIRAGIRA / appearance] which was mentioned above since these ingredients had the comparatively low light reflection factor was not given.

[0010] However, since [of a near-infrared region] it was in a long wavelength side comparatively, reflection and the absorption effect of these film in the near-infrared region near the light did not yet have enough plasma wave length.

[0011] Then, about the above-mentioned tin content indium oxide (ITO), the proposal which deoxidation processing is carried out [proposal] by the following approaches, and makes reflection and the absorption effect of the film in a near-infrared region improve is made. for example, the approach the method of heat-treating tin content indium oxide (ITO) in pressurization inert gas in JP,7-70481,A heat-treats tin content indium oxide (ITO) in alcoholic content nitrogen gas in JP,8-41441,A -- moreover, the method of heat-treating tin content indium oxide (ITO) in inert gas or reducibility gas in JP,10-120946,A is proposed.

[0012] However, by these approaches, the heating processing time was all as long as several hours, and the technical problem existed in productivity.

[0013] The place which this invention was made paying attention to such a trouble, and is made into the technical problem The Hayes value the particle for solar radiation screen formation which can form the solar radiation screen whose solar radiation permeability at the time of 80% or more of light permeability is moreover less than 1% at less than 70% The manufacture approach of the particle for solar radiation screen formation which can be manufactured conventionally in a short time, It is in offering the coating liquid for solar radiation screen formation using the particle obtained by this manufacture approach.

[0014] Then, the place which performed heat-treatment which this invention persons mixed the tungstic-acid ghost particle or the rhenium oxide particle to the above-mentioned tin content indium oxide particle, i.e., an indium stannic acid ghost particle, and was mentioned above in order to attain this purpose, While finding out that the above-mentioned heating processing time under a specific gas ambient atmosphere can be sharply shortened by the catalysis of a tungstic-acid ghost particle or a rhenium oxide particle By mixing with an indium stannic acid ghost particle with few amounts of residual impurities which consist of a chlorine ion, nitrate ion, and sulfate ion, a tungstic-acid ghost particle, or a rhenium oxide particle, said effectiveness finds out increasing further and came to complete this invention.

[0015]

[Means for Solving the Problem] Namely, invention concerning claim 1 is premised on the manufacture approach of the particle for solar radiation screen formation. Under the inert gas ambient atmosphere in which a mean diameter mixes an indium stannic acid ghost particle, a tungstic-acid ghost particle, or a rhenium oxide particle 100nm or less, and contains alcohol, Or invention which is characterized by heat-treating under the mixed-gas ambient atmosphere of reducibility gas and inert gas, and relates to claim 2 It is premised on the manufacture approach of the particle for solar radiation screen formation. Mean particle diameter by 100nm or less And the chlorine ion contained in a particle, The indium stannic acid ghost particle, tungstic-acid ghost particle, or rhenium oxide particle whose amount of residual impurities which consists of nitrate ion and sulfate ion is 0.6 or less % of the weight is mixed. It is characterized by heat-treating under the inert gas ambient atmosphere containing inert gas or alcohol, or the mixed-gas ambient atmosphere of reducibility gas and inert gas.

[0016] Moreover, invention concerning claim 3 is premised on the manufacture approach of the particle for solar radiation screen formation according to claim 1 or 2. Invention which the mixed rate of the above-mentioned indium stannic acid ghost particle and a tungstic-acid ghost particle is characterized by being 99.9:0.1-80:20 in a weight ratio, and requires it for claim 4 The mixed rate of the above-mentioned indium stannic acid ghost particle and a rhenium oxide particle is characterized by being 99.9:0.1-99:1 in a weight ratio a premise [the manufacture approach of the particle for solar radiation screen formation according to claim 1 or

2].

[0017] Next, invention concerning claim 5 relates to the coating liquid for solar radiation screen formation with which the particle for solar radiation screen formation obtained by the manufacture approaches, such as this, was applied. [0018] That is, invention concerning claim 5 is characterized by containing the particle for solar radiation screen formation according to claim 1 to 4, a solvent, and a binder on the assumption that the coating liquid for solar radiation screen formation.

[0019]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained to a detail.

[0020] First, the manufacture approach of the particle for solar radiation screen formation concerning this invention Under the inert gas ambient atmosphere which contains alcohol after a mean diameter mixes an indium stannic acid ghost particle, a tungstic-acid ghost particle, or a rhenium oxide particle 100nm or less, Or other manufacture approaches of the particle for solar radiation screen formation which is characterized by heat-treating under the mixed-gas ambient atmosphere of reducibility gas and inert gas (claim 1), and starts this invention Mean particle diameter by 100nm or less And the chlorine ion, nitrate ion which are contained in a particle, After the amount of residual impurities which consists of sulfate ion mixes the indium stannic acid ghost particle, tungstic-acid ghost particle, or rhenium oxide particle which is 0.6 or less % of the weight, It is characterized by heat-treating under the inert gas ambient atmosphere containing inert gas or alcohol, or the mixed-gas ambient atmosphere of reducibility gas and inert gas (claim 2). In addition, the mean particle diameter of the above-mentioned indium stannic acid ghost particle shows the mean particle diameter of the particle observed with a transmission electron microscope (TEM).

[0021] The particle obtained by approaches, such as this, is distributed in a solvent and a binder, and it considers as the coating liquid for solar radiation screen formation. In the indium stannic acid ghost particle to mix, the tin content in element conversion has 1 - 15 desirable % of the weight. It is because dissolving [of tin] may become inadequate at less than 1 % of the weight if the addition effectiveness of tin is not seen but it exceeds 15 % of the weight.

[0022] Moreover, the mean particle diameter of an indium stannic acid ghost particle needs to be 100nm or less, as mentioned above. It is because it becomes a source of light scattering, and cloudiness (Hayes) will be produced on the film or it will become the cause by which light permeability decreases, if mean particle diameter exceeds 100nm. In addition, although the magnitude of a particle is expressed with mean particle diameter here, the minimum available particle size is an about 2nm particle economically [the narrow fines of particle size distribution with few rates of coarse powder which exceeds 100nm are desirable, and]. However, the minimum of the above-mentioned particle size is not limited to this.

[0023] Next, if a tungsten is an oxide, which gestalt will be sufficient, for example, WO₃, WO₂, etc. will be mentioned.

[0024] moreover, the mixed rate of an indium stannic acid ghost particle and a tungstic-acid ghost particle -- the viewpoint of processing effectiveness and an optical property to a weight ratio -- 99.9:0.1-80:20 -- it is good to set it as the range of 99:1-85:15 preferably. It is because a solar radiation electric shielding property may get worse although the addition effectiveness of a tungsten is demonstrated even if the addition effectiveness is not acquired and it exceeds 20% if a tungstic-acid ghost particle is less than 0.1%.

[0025] On the other hand, if the above-mentioned rhenium is an oxide, which gestalt will be sufficient, for example, ReO₃, ReO₂, Re₂O₇, etc. will be mentioned.

[0026] Moreover, the mixed rate of an indium stannic acid ghost particle and a rhenium oxide particle is good to set it as the range of 99.9:0.1-99:1 by the weight ratio from a viewpoint of processing effectiveness and an optical property. It is because a solar radiation electric shielding property may get worse although the addition effectiveness of a tungsten is demonstrated even if the addition effectiveness is not acquired and it exceeds 1% if a rhenium oxide particle is less than 0.1%.

[0027] Next, the mixed approach of an indium stannic acid ghost particle, a tungstic-acid ghost particle, or a rhenium oxide particle will not be limited especially if mixable to homogeneity, but it can adopt a well-known approach.

[0028] Moreover, the heat-treatment to mixture with an indium stannic acid ghost particle, a tungstic-acid ghost particle, or a rhenium oxide particle When the amount of residual impurities which consists of the chlorine ion contained in an indium stannic acid ghost particle, nitrate ion, and sulfate ion is 0.6 % of the weight or more It

makes inert gas independent, such as nitrogen, an argon, and helium, into carrier gas. Or nitrogen, Feed of the alcohol is carried out by making mixed gas, such as an argon and helium, into carrier gas, or feed of the mixed gas of reducibility gas, such as hydrogen and a carbon monoxide, and said inert gas is carried out. Moreover, when the amount of residual impurities which consists of the chlorine ion contained in an indium stannic acid ghost particle, nitrate ion, and sulfate ion is below 0.6% weight, feed of the alcohol is carried out by making these mixed gas into carrier gas, carrying out feed by inert gas independent, such as nitrogen, an argon, and helium, or using said inert gas independent as carrier gas, or feed of the mixed gas of reducibility gas, such as hydrogen and a carbon monoxide, and said inert gas is carried out.

[0029] Moreover, although especially the alcohol to apply is not limited, a methanol, ethanol, its propanol, etc. are desirable from a viewpoint of volatility and cost. What is necessary is just to choose suitably each concentration and the amount of feed of the alcohol in inert gas, hydrogen, and a carbon monoxide so that the optical property considered as processing effectiveness or a request may be obtained.

[0030] Next, as for processing temperature, it is desirable that it is the range of 200-400 degrees C. It is because condensation and sintering of the above-mentioned oxide particle tend to take place and the addition effectiveness of a tungstic-acid ghost or a rhenium oxide particle may not be enough demonstrated at less than 200 degrees C, although the addition effectiveness of a tungstic-acid ghost or a rhenium oxide particle is demonstrated even if it exceeds 400 degrees C. Moreover, the heating processing time takes an ambient atmosphere and temperature into consideration, and is chosen suitably.

[0031] Since impurities, such as a chlorine ion which remains in an indium stannic acid ghost particle, nitrate ion, and sulfate ion, may serve as reduction inhibitor to deoxidation processing of the above-mentioned indium stannic acid ghost particle, its 0.3 or less % of the weight is preferably good 0.6 or less % of the weight. The addition effectiveness of a tungstic-acid ghost or a rhenium oxide particle is further demonstrated by mixing the indium stannic acid ghost particle, tungstic-acid ghost particle, or rhenium oxide particle whose amount of residual impurities which consists of a chlorine ion, nitrate ion, and sulfate ion as mentioned above is 0.6 or less % of the weight.

[0032] Next, although the coating liquid for solar radiation screen formation distributes the above-mentioned indium stannic acid ghost particle in a solvent and a binder, especially a solvent is not limited and is suitably chosen according to spreading conditions, a spreading environment, and an inorganic binder and a resin binder. For example, it is usable, and if needed, various kinds of organic solvents called ketones, such as ether, such as alcohols, such as water, ethanol, propanol, a butanol, isopropyl alcohol, isobutyl alcohol, and diacetone alcohol, methyl ether, ethyl ether, and pro PIRUE-Tell, ester, an acetone, a methyl ethyl ketone, a diethyl ketone, a cyclohexanone, and an isobutyl ketone, may add an acid and alkali, and may carry out pH adjustment. Furthermore, in order to raise the distributed stability of the particle in coating liquid further, of course, addition of various kinds of surfactants, a coupling agent, etc. is also possible.

[0033] Although especially the class of the above-mentioned inorganic binder or resin binder is not limited, as an inorganic binder, a metal alkoxide, and these partial hydrolysis condensation polymerization objects or the ORGANO silazane of silicon, a zirconium, titanium, or aluminum can use thermosetting resin, such as thermoplastics, such as acrylic resin, and an epoxy resin, etc. as a resin binder.

[0034] Especially if the distributed approach of an indium stannic acid ghost particle is the approach of distributing to homogeneity in coating liquid, it will not be limited, for example, a bead mill, a ball mill, a sand mill, a paint shaker, an ultrasonic homogenizer, etc. are mentioned.

[0035] In order to make the further ultraviolet-rays electric shielding function of a solar radiation screen give, one sort, such as particles, such as titanium oxide of an inorganic system, and a zinc oxide, cerium oxide, a benzophenone of an organic system, and benzotriazol, or two sorts or more may be added.

[0036]

[Example] Hereafter, an example explains this invention more concretely. However, this invention is not limited to the following examples.

[0037] In addition, the membranous light permeability and membranous solar radiation permeability which were obtained were measured using the spectrophotometer U-4000 by Hitachi, Ltd. moreover, the Hayes value - the Murakami Color Research Laboratory make -- it measured using HR-200. Membranes were formed by three sorts of bar coating machines from which a wire size differs in film evaluation, the light permeability of three kinds of film with which the thickness obtained by these differs, solar radiation permeability, and the

Hayes value were measured, respectively, and the solar radiation permeability and the Hayes value at the time of 86% of light permeability were calculated as a interpolation value from these three-point plots.

[0038] 10 % of the weight of [example 1] tin contents, the 0.7 % of the weight of the amounts of residual impurities, and the mixed rate of the indium stannic acid ghost particle [the Sumitomo Metal Mining [Co., Ltd.] Co., Ltd. make] of 0.03 micrometers of mean diameters and a tungstic trioxide particle were set to 99:1 by the weight ratio, and it mixed for 30 minutes.

[0039] Feed of the methanol content nitrogen carrier gas was carried out, it was heated, having put this into the 500ml separable flask, and stirring it, and the indium stannic acid ghost particle which is processed at the temperature of 300 degrees C for 9 minutes and by which the tungstic trioxide was added was obtained.

[0040] The paint shaker distributed the 20 % of the weight of the above-mentioned particles, 63.3 % of the weight of methyl isobutyl ketone, 16.7 % of the weight of dispersants, and 0.3mm zirconia beads equivalent to 63% of filling factors for 24 hours.

[0041] Next, after applying to a 100mmx100mmx3mm soda lime glass substrate the coating liquid which consists of the 67.5 % of the weight of the above-mentioned dispersion liquid, 27.5 % of the weight of acrylic resin solutions which dissolved in methyl isobutyl ketone as binders, and 5 % of the weight of curing agents by bar No.40, No.24, and No.6, respectively, it calcinated at 180 degrees C for 30 minutes, and the solar radiation screen a was obtained. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen a are shown in the following table 1.

[0042] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen a concerning an example 1 were 67.0% and 0.62%, respectively.

[0043] The solar radiation screen b concerning the example 2 as well as an example 1 was obtained except having set the mixed rate of a [example 2] indium stannic acid ghost particle and a tungstic trioxide particle to 98:2 by the weight ratio. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen b are shown in the following table 1.

[0044] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen b concerning an example 2 were 68.0% and 0.80%, respectively.

[0045] The solar radiation screen c concerning the example 3 as well as an example 1 was obtained except having set the mixed rate of a [example 3] indium stannic acid ghost particle and a tungstic trioxide particle to 96:4 by the weight ratio. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen c are shown in the following table 1.

[0046] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen c concerning an example 3 were 67.1% and 0.60%, respectively.

[0047] The solar radiation screen d concerning the example 4 as well as an example 1 was obtained except having set the mixed rate of a [example 4] indium stannic acid ghost particle and a tungstic trioxide particle to 88:12 by the weight ratio. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen d are shown in the following table 1.

[0048] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen d concerning an example 4 were 67.0% and 0.35%, respectively.

[0049] The solar radiation screen e concerning the example 5 as well as an example 1 was obtained except having set the mixed rate of a [example 5] indium stannic acid ghost particle and a tungstic trioxide particle to 82:18 by the weight ratio. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen e are shown in the following table 1.

[0050] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen e concerning an example 5 were 68.9% and 0.75%, respectively.

[0051] Since solar radiation permeability was 70% or more on the conditions which do not add the [example 1 of comparison] tungstic trioxide when the above-mentioned indium stannic acid ghost particle is heat-treated for 9 minutes at 300 degrees C, the processing time was made into 60 minutes and the solar radiation screen f which starts the example 1 of a comparison like an example 1 was obtained except it. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen f are shown in the following table 1.

[0052] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen f concerning the example 1 of a comparison were 66.0% and 0.40%, respectively.

[0053] On the conditions which do not add the [example 2 of comparison] tungstic trioxide, the processing time

was made into 180 minutes and the solar radiation screen g which starts the example 2 of a comparison like an example 1 was obtained except it. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen g are shown in the following table 1.

[0054] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen g concerning the example 2 of a comparison were 66.5% and 0.46%, respectively.

[0055] In order to obtain the solar radiation screen concerning each example, and the solar radiation screen which has the same property as a result of this etc., it was checked that it is necessary to set the processing time for 60 minutes longer than for [of each example] 9 minutes and as for 180 minutes.

[0056] The solar radiation screen h concerning the example 6 as well as an example 1 was obtained except having made [example 6] processing temperature into 350 degrees C. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen h are shown in the following table 1.

[0057] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen h concerning an example 6 were 68.1% and 0.35%, respectively.

[0058] The solar radiation screen i concerning the example 7 as well as an example 1 was obtained using 5%H₂ gas which replaced with [example 7] methanol content nitrogen carrier gas, and used N₂ as the carrier except having processed at 300 degrees C for 60 minutes. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen i are shown in the following table 1.

[0059] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen i concerning an example 7 were 66.0% and 0.63%, respectively.

[0060] Since solar radiation permeability was 70% or more on the conditions which do not add the [example 3 of comparison] tungstic trioxide when the above-mentioned indium stannic acid ghost particle is heat-treated for 60 minutes at 300 degrees C, the processing time was made into 480 minutes and the solar radiation screen j which starts the example 3 of a comparison like an example 7 was obtained except it. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen j are shown in the following table 1.

[0061] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen j concerning the example 3 of a comparison were 67.1% and 0.46%, respectively.

[0062] Consequently, in order to obtain the solar radiation screen i concerning an example 7, and the solar radiation screen which has the same property, it was checked that it is necessary to set the processing time as for 480 minutes longer than for [of an example 7] 60 minutes.

[0063] 10 % of the weight of [example 8] tin contents, the 0.1 % of the weight of the amounts of residual impurities, and the mixed rate of the indium stannic acid ghost particle [the Sumitomo Metal Mining [Co., Ltd.] Co., Ltd. make] of 0.03 micrometers of mean diameters and a tungstic trioxide particle were set to 99:1 by the weight ratio, feed of the methanol content nitrogen carrier gas was carried out, it was heated, and the solar radiation screen k concerning the example 8 as well as an example 1 was obtained except having processed at 300 degrees C for 3 minutes. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen k are shown in the following table 1.

[0064] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen k concerning an example 8 were 66.7% and 0.58%, respectively.

[0065] [Example 9] The solar radiation screen l concerning the example 9 as well as an example 8 was obtained except having processed N₂ at 260 degrees C for 40 minutes using 5%H₂ gas used as the carrier. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen l are shown in the following table 1.

[0066] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen l concerning an example 9 were 69.9% and 0.90%, respectively.

[0067] The solar radiation screen m concerning the example 10 as well as an example 8 was obtained using [example 10] N₂ gas except having processed at 300 degrees C for 10 minutes. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen m are shown in the following table 1.

[0068] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen m concerning an example 10 were 69.8% and 0.64%, respectively.

[0069] Since solar radiation permeability was 70% or more on the conditions using [example 4 of comparison] N₂ gas when 10 % of the weight of tin contents, the 0.7 % of the weight of the amounts of residual impurities, and the indium stannic acid ghost particle [the Sumitomo Metal Mining [Co., Ltd.] Co., Ltd. make] of 0.03

micrometers of mean diameters are heat-treated for 9 minutes at 300 degrees C, the processing time was made into 60 minutes and the solar radiation screen n which starts the example 4 of a comparison like an example 1 was obtained except it. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen n are shown in the following table 1.

[0070] And as checked from this table 1, the solar radiation permeability and the Hayes values of the solar radiation screen n concerning the example 4 of a comparison were 69.6% and 0.60%, respectively.

[0071] Consequently, in order to obtain the solar radiation screen which has 10 % of the weight of tin contents, the 0.1 % of the weight of the amounts of residual impurities, and the same property as the solar radiation screen m concerning the example 10 to which the indium stannic acid ghost particle of 0.03 micrometers of mean diameters was applied, it was checked that it is necessary to set the processing time as for 60 minutes longer than for [of an example 10] 10 minutes.

[0072]

[Table 1]

ITO:WO ₃ (重量%)	雰囲気	処理温度 (°C)	処理時間 (分)		可視光透過率 8 6 % 固定	
					日射透過率 (%)	ヘイズ値 (%)
実施例 1 99 : 1	1%I-1%N ₂	300	9	膜 a	67.0	0.62
実施例 2 98 : 2	1%I-1%N ₂	300	9	膜 b	68.0	0.80
実施例 3 96 : 4	1%I-1%N ₂	300	9	膜 c	67.1	0.60
実施例 4 88 : 12	1%I-1%N ₂	300	9	膜 d	67.0	0.35
実施例 5 82 : 18	1%I-1%N ₂	300	9	膜 e	68.9	0.75
比較例 1 100 : 0	1%I-1%N ₂	300	60	膜 f	66.0	0.40
比較例 2 100 : 0	1%I-1%N ₂	300	180	膜 g	66.5	0.46
実施例 6 99 : 1	1%I-1%N ₂	350	9	膜 h	68.1	0.36
実施例 7 99 : 1	5%H ₂ /N ₂	300	60	膜 i	66.0	0.63
比較例 3 100 : 0	5%H ₂ /N ₂	300	480	膜 j	67.1	0.46
実施例 8 99 : 1	1%I-1%N ₂	300	3	膜 k	66.7	0.58
実施例 9 99 : 1	5%H ₂ /N ₂	260	40	膜 l	69.9	0.90
実施例 10 99 : 1	N ₂	300	10	膜 m	69.8	0.64
比較例 4 99 : 1	N ₂	300	60	膜 n	69.6	0.60

10 % of the weight of [example 11] tin contents, the 0.7 % of the weight of the amounts of residual impurities, and the mixed rate of the indium stannic acid ghost particle [the Sumitomo Metal Mining [Co., Ltd.] Co., Ltd. make] of 0.03 micrometers of mean diameters and a 3 rhenium-oxide particle were set to 99.5:0.5 by the weight ratio, and it mixed for 30 minutes.

[0073] Feed of the methanol content nitrogen carrier gas was carried out, it was heated, having put this into the 500ml separable flask, and stirring it, and the indium stannic acid ghost particle which is processed at the temperature of 300 degrees C for 7 minutes and by which 3 rhenium oxide was added was obtained.

[0074] The paint shaker distributed the 20 % of the weight of the above-mentioned particles, 63.3 % of the weight of methyl isobutyl ketone, 16.7 % of the weight of dispersants, and 0.3mm zirconia beads equivalent to 63% of filling factors for 24 hours.

[0075] Next, after applying to a 100mmx100mmx3mm soda lime glass substrate the coating liquid which consists of the 67.5 % of the weight of the above-mentioned dispersion liquid, 27.5 % of the weight of acrylic resin solutions which dissolved in methyl isobutyl ketone as binders, and 5 % of the weight of curing agents by bar No.40, No.24, and No.6, respectively, it calcinated at 180 degrees C for 30 minutes, and the solar radiation screen o was obtained. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen o are shown in the following table 2.

[0076] And as checked from this table 2, the solar radiation permeability and the Hayes values of the solar radiation screen o concerning an example 11 were 67.7% and 0.30%, respectively.

[0077] The solar radiation screen p concerning the example 12 as well as an example 11 was obtained except having set the mixed rate of a [example 12] indium stannic acid ghost particle and a 3 rhenium-oxide particle to

99.9:0.1 by the weight ratio. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen p are shown in the following table 2.

[0078] And as checked from this table 2, the solar radiation permeability and the Hayes values of the solar radiation screen p concerning an example 12 were 67.5% and 0.30%, respectively.

[0079] The solar radiation screen q concerning the example 13 as well as an example 11 was obtained except having set the mixed rate of a [example 13] indium stannic acid ghost particle and a 3 rhenium-oxide particle to 99.2:0.8 by the weight ratio. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen q are shown in the following table 2.

[0080] And as checked from this table 2, the solar radiation permeability and the Hayes values of the solar radiation screen q concerning an example 13 were 68.5% and 0.29%, respectively.

[0081] Since solar radiation permeability was 70% or more on the conditions which do not add [example 5 of comparison] 3 rhenium oxide when the above-mentioned indium stannic acid ghost particle is heat-treated for 7 minutes at 300 degrees C, the processing time was made into 60 minutes and the solar radiation screen r which starts the example 5 of a comparison like an example 11 was obtained except it. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen r are shown in the following table 2.

[0082] And as checked from this table 2, the solar radiation permeability and the Hayes values of the solar radiation screen r concerning the example 5 of a comparison were 66.0% and 0.40%, respectively.

[0083] On the conditions which do not add [example 6 of comparison] 3 rhenium oxide, the processing time was made into 180 minutes and the solar radiation screen s which starts the example 6 of a comparison like an example 11 was obtained except it. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen s are shown in the following table 2.

[0084] And as checked from this table 2, the solar radiation permeability and the Hayes values of the solar radiation screen s concerning the example 6 of a comparison were 66.5% and 0.46%, respectively.

[0085] In order to obtain the solar radiation screen concerning examples 11-13, and the solar radiation screen which has the same property as a result of this etc., it was checked that it is necessary to set the processing time for 60 minutes longer than for [of each example] 7 minutes and as for 180 minutes.

[0086] The solar radiation screen t concerning the example 14 as well as an example 11 was obtained except having made [example 14] processing temperature into 350 degrees C. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen t are shown in the following table 2.

[0087] And as checked from this table 2, the solar radiation permeability and the Hayes values of the solar radiation screen t concerning an example 14 were 68.6% and 0.39%, respectively.

[0088] The solar radiation screen u concerning the example 15 as well as an example 11 was obtained using 5% H₂ gas which replaced with [example 15] methanol content nitrogen carrier gas, and used N₂ as the carrier except having processed at 300 degrees C for 60 minutes. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen u are shown in the following table 2.

[0089] And as checked from this table 2, the solar radiation permeability and the Hayes values of the solar radiation screen u concerning an example 15 were 66.8% and 0.29%, respectively.

[0090] Since solar radiation permeability was 70% or more on the conditions which do not add [example 7 of comparison] 3 rhenium oxide when the above-mentioned indium stannic acid ghost particle is heat-treated for 60 minutes at 300 degrees C, the processing time was made into 480 minutes and the solar radiation screen v which starts the example 7 of a comparison like an example 15 was obtained except it. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen v are shown in the following table 2.

[0091] And as checked from this table 2, the solar radiation permeability and the Hayes values of the solar radiation screen v concerning the example 7 of a comparison were 67.1% and 0.46%, respectively.

[0092] Consequently, in order to obtain the solar radiation screen u concerning an example 15, and the solar radiation screen which has the same property, it was checked that it is necessary to set the processing time as for 480 minutes longer than for [of an example 15] 60 minutes.

[0093] 10 % of the weight of [example 16] tin contents, the 0.1 % of the weight of the amounts of residual impurities, and the mixed rate of the indium stannic acid ghost particle [the Sumitomo Metal Mining [Co., Ltd.] Co., Ltd. make] of 0.03 micrometers of mean diameters and a 3 rhenium-oxide particle were set to 99.5:0.5 by the weight ratio, feed of the methanol content nitrogen carrier gas was carried out, it was heated, and the solar radiation screen w concerning the example 16 as well as an example 11 was obtained except

having processed at 270 degrees C for 40 minutes. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen w are shown in the following table 2.

[0094] And as checked from this table 2, the solar radiation permeability and the Hayes values of the solar radiation screen w concerning an example 16 were 69.5% and 0.42%, respectively.

[0095] The solar radiation screen x concerning the example 17 as well as an example 16 was obtained using [example 17] N₂ gas except having processed at 300 degrees C for 10 minutes. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen x are shown in the following table 2.

[0096] And as checked from this table 2, the solar radiation permeability and the Hayes values of the solar radiation screen x concerning an example 17 were 69.9% and 0.35%, respectively.

[0097] Since solar radiation permeability was 70% or more on the conditions using [example 8 of comparison] N₂ gas when 10 % of the weight of tin contents, the 0.7 % of the weight of the amounts of residual impurities, and the indium stannic acid ghost particle [the Sumitomo Metal Mining [Co., Ltd.] Co., Ltd. make] of 0.03 micrometers of mean diameters are heat-treated for 10 minutes at 300 degrees C, the processing time was made into 60 minutes and the solar radiation screen y which starts the example 8 of a comparison like an example 11 was obtained except it. The solar radiation permeability (%) and the Hayes value (%) of this solar radiation screen y are shown in the following table 2.

[0098] And as checked from this table 2, the solar radiation permeability and the Hayes values of the solar radiation screen y concerning the example 8 of a comparison were 69.6% and 0.33%, respectively.

[0099] Consequently, in order to obtain the solar radiation screen which has 10 % of the weight of tin contents, the 0.1 % of the weight of the amounts of residual impurities, and the same property as the solar radiation screen x concerning the example 17 to which the indium stannic acid ghost particle of 0.03 micrometers of mean diameters was applied, it was checked that it is necessary to set the processing time as for 60 minutes longer than for [of an example 17] 10 minutes.

[0100]

[Table 2]

	ITO: ReO ₃ (重量%)	雰囲気	処理温度 (°C)	処理時間 (分)		可視光透過率 8 6 % 固定	
						日射透過率 (%)	ヘイズ値 (%)
実施例11	99.5 : 0.5	Ar-N ₂	300	7	膜 a	67.7	0.30
実施例12	99.9 : 0.1	Ar-N ₂	300	7	膜 p	67.5	0.30
実施例13	99.2 : 0.8	Ar-N ₂	300	7	膜 q	68.5	0.29
比較例5	100 : 0	Ar-N ₂	300	60	膜 r	66.0	0.40
比較例6	100 : 0	Ar-N ₂	300	180	膜 s	66.5	0.46
実施例14	99.5 : 0.5	Ar-N ₂	350	7	膜 t	68.6	0.39
実施例15	99.5 : 0.5	5%H ₂ /N ₂	300	60	膜 u	66.8	0.29
比較例7	100 : 0	5%H ₂ /N ₂	300	480	膜 v	67.1	0.46
実施例16	99.5 : 0.5	Ar-N ₂	270	40	膜 w	69.5	0.42
実施例17	99.5 : 0.5	N ₂	300	10	膜 x	69.9	0.35
比較例8	99.5 : 0.5	N ₂	300	60	膜 y	69.6	0.33

[0101]

[Effect of the Invention] According to the manufacture approach of the particle for solar radiation screen formation concerning invention according to claim 1 to 4 By the catalysis of the tungstic-acid ghost particle added by the tin content indium oxide particle at the time of heat-treatment, or a rhenium oxide particle Moreover, the solar radiation permeability at the time of 80% or more of light permeability has the effectiveness that the particle for solar radiation screen formation which can form the solar radiation screen whose Hayes value is less than 1% can be manufactured conventionally in a short time, at less than 70%. Moreover, according to the coating liquid for solar radiation screen formation concerning invention according to claim 5, the solar radiation permeability at the time of 80% or more of light permeability has the effectiveness which can form the solar radiation screen whose Hayes value is less than 1% at less than 70%.

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(54) PRODUCING METHOD FOR FINE PARTICLE FOR FORMING INSOLATION SHIELDING FILM AND APPLICATION LIQUID FOR FORMING INSOLATION SHIELDING FILM USING THE FINE PARTICLE OBTAINED BY THE PRODUCING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a producing method for a fine particle for forming an insolation shielding film which produces fine particles for forming the insolation shielding film which is capable of forming insolation shielding film of which the insolation transmittance at visible light transmittance of $\geq 80\%$ is less than 70% and the haze value is less than 1% in a shorter time than the conventional method.

SOLUTION: This producing method of the fine particle for forming an insolation shielding film is characterized in that indium tin oxide fine particles the averaged grain size of which is < 100 nm and tungsten oxide fine particles or rhenium oxide fine particles are mixed and are heated and treated under an atmosphere of inactive gas including alcohol or an atmosphere of mixed gas of a reducing gas and an inactive gas and the fine particles for forming insolation shielding film can be produced in a shorter time than the conventional method thanks to the catalytic action of the tungsten oxide fine particles or rhenium oxide fine particles which are added to tin-containing indium oxide fine particles at the time of heat treatment.

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弁理士 上田 章三

最終頁に続く

(54) 【発明の名称】 日射遮蔽膜形成用微粒子の製造方法とこの製造方法により得られた微粒子を用いた日射遮蔽膜形成用塗布液

(57) 【要約】

【課題】 可視光透過率80%以上のときの日射透過率が70%未満でヘイズ値が1%未満である日射遮蔽膜を形成可能な日射遮蔽膜形成用微粒子を従来よりも短時間で製造できる日射遮蔽膜形成用微粒子の製造方法等を提供すること。

【解決手段】 この日射遮蔽膜形成用微粒子の製造方法は、平均粒径が100nm以下のインジウム錫酸化物微粒子とタングステン酸化物微粒子またはレニウム酸化物微粒子とを混合し、アルコールを含む不活性ガス雰囲気下または還元性ガスと不活性ガスとの混合ガス雰囲気下で加熱処理することとを特徴とし、加熱処理時において錫含有酸化インジウム微粒子に添加された上記タングステン酸化物微粒子またはレニウム酸化物微粒子の触媒作用により従来よりも短時間で日射遮蔽膜形成用微粒子を製造することが可能となる。

【特許請求の範囲】

【請求項1】日射遮蔽膜形成用微粒子の製造方法において、

平均粒径が100nm以下のインジウム錫酸化物微粒子とタングステン酸化物微粒子またはレニウム酸化物微粒子とを混合し、アルコールを含む不活性ガス雰囲気下、または、還元性ガスと不活性ガスとの混合ガス雰囲気下で加熱処理することを特徴とする日射遮蔽膜形成用微粒子の製造方法。

【請求項2】日射遮蔽膜形成用微粒子の製造方法において、

平均粒径が100nm以下でかつ粒子中に含まれる塩素イオン、硝酸イオン、硫酸イオンからなる残留不純物量が0.6重量%以下であるインジウム錫酸化物微粒子とタングステン酸化物微粒子またはレニウム酸化物微粒子とを混合し、不活性ガス若しくはアルコールを含む不活性ガス雰囲気下、または、還元性ガスと不活性ガスとの混合ガス雰囲気下で加熱処理することを特徴とする日射遮蔽膜形成用微粒子の製造方法。

【請求項3】上記インジウム錫酸化物微粒子とタングステン酸化物微粒子との混合割合が、重量比で99.9:0.1~80:20であることを特徴とする請求項1または2記載の日射遮蔽膜形成用微粒子の製造方法。

【請求項4】上記インジウム錫酸化物微粒子とレニウム酸化物微粒子との混合割合が、重量比で99.9:0.1~99:1であることを特徴とする請求項1または2記載の日射遮蔽膜形成用微粒子の製造方法。

【請求項5】請求項1~4のいずれかに記載の日射遮蔽膜形成用微粒子、溶媒およびバインダーを含有することを特徴とする日射遮蔽膜形成用塗布液。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、車両、ビル、事務所、一般住宅などの窓材、電話ボックス、ショーウィンドー、照明用ランプ、透明ケースなど、ガラス、プラスチックその他の日射遮蔽機能が必要とする透明基材に適用される日射遮蔽膜形成用微粒子に係り、特に、可視光透過率80%以上のときの日射透過率が70%未満でしかもヘイズ値が1%未満である日射遮蔽膜を形成可能な日射遮蔽膜形成用微粒子の製造方法と、この製造方法により得られた微粒子を用いた日射遮蔽膜形成用塗布液に関するものである。

【0002】

【従来の技術】太陽光や電球などの外部光源から熱成分を除去・減少する方法として、従来、ガラス表面に可視・赤外域の波長を反射する材料を成膜して熱線反射ガラスとする方法が行われている。そして、上記材料としては、 FeOx 、 CoOx 、 CrOx 、 TiOx などの金属酸化物や、 Ag 、 Au 、 Cu 、 Ni 、 Al など自由電子を多量にもつ金属材料が選択されてきた。

【0003】しかし、これらの材料には、熱効果に大きく寄与する近赤外線以外に可視光も同時に反射もしくは吸収する性質があるため、可視光透過率が低下する問題があった。そして、建材、乗り物、電話ボックスなどに用いられる透明基材では可視光領域の高い透過率が必要とされることから、前記材料を利用する場合は膜厚を非常に薄くしなければならない。従って、スプレー焼付けやCVD法、あるいはスパッタ法や真空蒸着法などの物理成膜法を用いて10nmレベルの薄膜に成膜して用いられることが通常行われている。そして、これらの成膜方法は大きな装置や真空設備を必要とし、生産性や大面積化に問題があるため膜の製造コストが高いといった欠点があった。

【0004】また、上記成膜法を用いて膜厚を薄くし可視光の透過率を高くしようとすると膜の日射遮蔽特性が低下し、反対に膜厚を厚くして日射遮蔽特性を高くすると膜が暗くなってしまう問題もあった。

【0005】また、これらの材料で日射遮蔽特性を高くしようとすると可視光領域の反射率も同時に高くなってしまいう傾向があり、鏡のようなギラギラした外観を与えて美観を損ねてしまう問題点も存在した。

【0006】更に、これらの材料では膜の導電性が高くなるものが多い。そして、膜の導電性が高いと携帯電話やTV、ラジオなどの電波を反射して受信不能になったり、周辺地域に電波障害を引き起こすなどの問題もあった。

【0007】一方、フタロシアニン系や金属錯体系などの有機系近赤外線吸収剤をバインダー中に添加した樹脂フィルムも使用されている。しかし、無機系の材料に比べて熱や湿度による劣化が顕著であり、耐候性に欠点があった。

【0008】このような従来の日射遮蔽膜の欠点を改善するためには、膜の物理特性として可視光領域の光の反射率が低くて透過率が高く、かつ、赤外線領域の透過率が低いと共に、膜の導電性が概ね $10^6 \Omega/\square$ 以上に制御可能な膜を形成できることが必要であった。

【0009】

【発明が解決しようとする課題】ところで、可視光透過率が高くしかも日射遮蔽機能を持つ材料として、アンチモン含有酸化錫(ATO)や錫含有酸化インジウム(ITO)も知られており、これら材料は可視光反射率が比較的低いため上述したギラギラした外観を与えることはなかった。

【0010】但し、プラズマ波長が近赤外域の比較的長波長側にあることから、可視光に近い近赤外域におけるこれらの膜の反射・吸収効果は未だ十分でなかった。

【0011】そこで、上記錫含有酸化インジウム(ITO)については以下の方法により脱酸素処理して近赤外域における膜の反射・吸収効果を改善させる提案がなされている。例えば、特開平7-70481号公報におい

て錫含有酸化インジウム（ITO）を加圧不活性ガス中で加熱処理する方法が、特開平 8-41441 号公報において錫含有酸化インジウム（ITO）をアルコール含有窒素ガス中で加熱処理する方法が、また、特開平 10-120946 号公報において錫含有酸化インジウム（ITO）を不活性ガスあるいは還元性ガス中で加熱処理する方法が提案されている。

【0012】しかし、これらの方法ではいずれも加熱処理時間が数時間と長く、生産性に課題が存在した。

【0013】本発明はこのような問題点に着目してなされたもので、その課題とするところは、可視光透過率 80% 以上のときの日射遮蔽率が 70% 未満でしかもヘイズ値が 1% 未満である日射遮蔽膜を形成可能な日射遮蔽膜形成用微粒子を従来よりも短時間で製造可能な日射遮蔽膜形成用微粒子の製造方法と、この製造方法により得られた微粒子を用いた日射遮蔽膜形成用塗布液を提供することにある。

【0014】そこで、この目的を達成するため、本発明者らは上記錫含有酸化インジウム微粒子すなわちインジウム錫酸化物微粒子に対しタングステン酸化物微粒子またはレニウム酸化物微粒子を混合して上述した加熱処理を施したところ、タングステン酸化物微粒子またはレニウム酸化物微粒子の触媒作用により特定ガス雰囲気下での上記加熱処理時間が大幅に短縮できることを見出すと共に、塩素イオン、硝酸イオン、硫酸イオンからなる残留不純物量の少ないインジウム錫酸化物微粒子とタングステン酸化物微粒子またはレニウム酸化物微粒子との混合によって前記効果が一層増すことを見出して本発明を完成するに至った。

【0015】

【課題を解決するための手段】すなわち、請求項 1 に係る発明は、日射遮蔽膜形成用微粒子の製造方法を前提とし、平均粒径が 100 nm 以下のインジウム錫酸化物微粒子とタングステン酸化物微粒子またはレニウム酸化物微粒子とを混合し、アルコールを含む不活性ガス雰囲気下、または、還元性ガスと不活性ガスとの混合ガス雰囲気下で加熱処理することの特徴とし、請求項 2 に係る発明は、日射遮蔽膜形成用微粒子の製造方法を前提とし、平均粒径が 100 nm 以下でかつ粒子中に含まれる塩素イオン、硝酸イオン、硫酸イオンからなる残留不純物量が 0.6 重量% 以下であるインジウム錫酸化物微粒子とタングステン酸化物微粒子またはレニウム酸化物微粒子とを混合し、不活性ガス若しくはアルコールを含む不活性ガス雰囲気下、または、還元性ガスと不活性ガスとの混合ガス雰囲気下で加熱処理することの特徴とする。

【0016】また、請求項 3 に係る発明は、請求項 1 または 2 記載の日射遮蔽膜形成用微粒子の製造方法を前提とし、上記インジウム錫酸化物微粒子とタングステン酸化物微粒子との混合割合が、重量比で 99.9 : 0.1 ~ 80 : 20 であることを特徴とし、請求項 4 に係る発

明は、請求項 1 または 2 記載の日射遮蔽膜形成用微粒子の製造方法を前提とし、上記インジウム錫酸化物微粒子とレニウム酸化物微粒子との混合割合が、重量比で 99.9 : 0.1 ~ 99 : 1 であることを特徴とするものである。

【0017】次に、請求項 5 に係る発明はこれ等製造方法にて得られた日射遮蔽膜形成用微粒子が適用された日射遮蔽膜形成用塗布液に関する。

【0018】すなわち、請求項 5 に係る発明は、日射遮蔽膜形成用塗布液を前提とし、請求項 1 ~ 4 のいずれかに記載の日射遮蔽膜形成用微粒子、溶媒およびバインダーを含有することを特徴とするものである。

【0019】

【発明の実施の形態】以下、本発明の実施の形態について詳細に説明する。

【0020】まず、本発明に係る日射遮蔽膜形成用微粒子の製造方法は、平均粒径が 100 nm 以下のインジウム錫酸化物微粒子とタングステン酸化物微粒子またはレニウム酸化物微粒子とを混合した後、アルコールを含む不活性ガス雰囲気下、または、還元性ガスと不活性ガスとの混合ガス雰囲気下で加熱処理することの特徴とし

（請求項 1）、また、本発明に係る日射遮蔽膜形成用微粒子の他の製造方法は、平均粒径が 100 nm 以下でかつ粒子中に含有する塩素イオン、硝酸イオン、硫酸イオンからなる残留不純物量が 0.6 重量% 以下であるインジウム錫酸化物微粒子とタングステン酸化物微粒子またはレニウム酸化物微粒子とを混合した後、不活性ガス若しくはアルコールを含む不活性ガス雰囲気下、または、還元性ガスと不活性ガスとの混合ガス雰囲気下で加熱処理することの特徴（請求項 2）とする。尚、上記インジウム錫酸化物微粒子の平均粒径とは、透過電子顕微鏡（TEM）で観察される微粒子の平均粒径を示している。

【0021】これ等方法で得られた微粒子を溶媒およびバインダー中に分散して日射遮蔽膜形成用塗布液とする。混合するインジウム錫酸化物微粒子において、元素換算での錫含有量は 1 ~ 15 重量% が好ましい。1 重量% 未満では錫の添加効果が見られず、15 重量% を超えると錫の固溶が不十分となる場合があるからである。

【0022】また、インジウム錫酸化物微粒子の平均粒径は、上述したように 100 nm 以下であることが必要である。平均粒径が 100 nm を超えると光散乱源となって膜に曇り（ヘイズ）を生じたり、可視光透過率が減少する原因になるからである。尚、ここでは粒子の大きさを平均粒径で表しているが、100 nm を超えるような粗粉の割合が少なく粒度分布の狭い微粉が好ましく、かつ、経済的に入手可能な最低の粒径は 2 nm 程度の微粒子である。但し、上記粒径の下限をこれに限定するものではない。

【0023】次に、タングステンは酸化物であればい

れの形態でもよく、例えば WO_3 や WO_2 などが挙げられる。

【0024】また、インジウム錫酸化物微粒子とタングステン酸化物微粒子との混合割合は、処理効率と光学特性の観点から重量比で99.9:0.1~80:20、好ましくは99:1~85:15の範囲に設定するとよい。タングステン酸化物微粒子が0.1%未満だと添加効果が得られず、また、20%を超えてもタングステンの添加効果は発揮されるが日射遮蔽特性が悪化してくる場合があるからである。

【0025】他方、上記レニウムは酸化物であればいずれの形態でもよく、例えば ReO_3 、 ReO_2 、 Re_2O_7 などが挙げられる。

【0026】また、インジウム錫酸化物微粒子とレニウム酸化物微粒子との混合割合は、処理効率と光学特性の観点から重量比で99.9:0.1~99:1の範囲に設定するとよい。レニウム酸化物微粒子が0.1%未満だと添加効果が得られず、また、1%を超えてもタングステンの添加効果は発揮されるが日射遮蔽特性が悪化してくる場合があるからである。

【0027】次に、インジウム錫酸化物微粒子とタングステン酸化物微粒子またはレニウム酸化物微粒子の混合方法は均一に混合できれば特に限定されず、公知の方法を採用できる。

【0028】また、インジウム錫酸化物微粒子とタングステン酸化物微粒子またはレニウム酸化物微粒子との混合物に対する加熱処理は、インジウム錫酸化物微粒子中に含有する塩素イオン、硝酸イオン、硫酸イオンからなる残留不純物量が0.6重量%以上の場合は、窒素、アルゴン、ヘリウムなどの不活性ガス単独をキャリアガスとして若しくは窒素、アルゴン、ヘリウムなどの混合ガスをキャリアガスとしてアルコールをフィードするか、または、水素や一酸化炭素などの還元性ガスと前記不活性ガスとの混合ガスをフィードする。また、インジウム錫酸化物微粒子中に含有する塩素イオン、硝酸イオン、硫酸イオンからなる残留不純物量が0.6重量%以下の場合は、窒素、アルゴン、ヘリウムなどの不活性ガス単独でフィードするか、前記不活性ガス単独をキャリアガスとして若しくはこれらの混合ガスをキャリアガスとしてアルコールをフィードするか、または、水素や一酸化炭素などの還元性ガスと前記不活性ガスとの混合ガスをフィードする。

【0029】また、適用するアルコールは特に限定されるものではないが、揮発性とコストの観点からメタノール、エタノール、プロパノールなどが好ましい。不活性ガス中のアルコール、水素、一酸化炭素の各濃度やフィード量は、処理効率や所望とする光学特性が得られるように適宜選択すればよい。

【0030】次に、処理温度は200~400℃の範囲であることが好ましい。400℃を超えてもタングステ

ン酸化物またはレニウム酸化物微粒子の添加効果は発揮されるが上記酸化物粒子の凝集・焼結が起こり易く、200℃未満ではタングステン酸化物またはレニウム酸化物微粒子の添加効果が十分発揮されない場合があるからである。また、加熱処理時間は雰囲気と温度を勘案して適宜選択される。

【0031】インジウム錫酸化物微粒子中に残留する塩素イオン、硝酸イオン、硫酸イオンなどの不純物は、上記インジウム錫酸化物微粒子の脱酸素処理に対して還元阻害因子となることがあるため、0.6重量%以下、好ましくは0.3重量%以下がよい。上述したように塩素イオン、硝酸イオン、硫酸イオンからなる残留不純物量が0.6重量%以下であるインジウム錫酸化物微粒子とタングステン酸化物微粒子またはレニウム酸化物微粒子とを混合することによってタングステン酸化物またはレニウム酸化物微粒子の添加効果が一層発揮される。

【0032】次に、日射遮蔽膜形成用塗布液は、上記インジウム錫酸化物微粒子を溶媒およびバインダー中に分散したものであるが、溶媒は特に限定されるものではなく、塗布条件、塗布環境、および無機バインダーや樹脂バインダーに合わせて適宜選択される。例えば、水やエタノール、プロパノール、ブタノール、イソプロピルアルコール、イソブチルアルコール、ジアセトンアルコールなどのアルコール類、メチルエーテル、エチルエーテル、プロピルエーテルなどのエーテル類、エステル類、アセトン、メチルエチルケトン、ジエチルケトン、シクロヘキサノン、イソブチルケトンなどのケトン類といった各種の有機溶媒が使用可能であり、また必要に応じて酸やアルカリを添加してpH調整してもよい。さらに、塗布液中の微粒子の分散安定性を一層向上させるためには、各種の界面活性剤、カップリング剤などの添加も勿論可能である。

【0033】上記無機バインダーや樹脂バインダーの種類は特に限定されるものではないが、無機バインダーとしては、珪素、ジルコニウム、チタン、もしくはアルミニウムの金属アルコキシドやこれらの部分加水分解縮重合物あるいはオルガノシラザンが、樹脂バインダーとしてはアクリル樹脂などの熱可塑性樹脂、エポキシ樹脂などの熱硬化性樹脂などが利用できる。

【0034】インジウム錫酸化物微粒子の分散方法は塗布液中に均一に分散する方法であれば特に限定されず、例えばビーズミル、ボールミル、サンドミル、ペイントシェーカー、超音波ホモジナイザーなどが挙げられる。

【0035】日射遮蔽膜のさらなる紫外線遮蔽機能を付与させるため、無機系の酸化チタンや酸化亜鉛、酸化セリウムなどの微粒子や、有機系のベンゾフェノンやベンゾトリアゾールなどの1種もしくは2種以上を添加してもよい。

【0036】

【実施例】以下、実施例により本発明をより具体的に説

明する。ただし、本発明は以下の実施例に限定されるものでない。

【0037】尚、得られた膜の可視光透過率や日射透過率は日立製作所（株）製の分光光度計U-4000を用いて測定した。また、ヘイズ値は村上色彩技術研究所（株）製HR-200を用いて測定した。膜評価においては線径の異なる3種のパーコーターで成膜し、これらにより得られた膜厚の異なる3種類の膜の可視光透過率、日射透過率、ヘイズ値をそれぞれ測定し、これらの3点プロットからの内挿値として可視光透過率86%の

【0038】【実施例1】錫含有量10重量%、残留不純物量0.7重量%、平均粒径0.03 μ mのインジウム錫酸化物微粒子〔住友金属鉱山（株）社製〕と三酸化タングステン微粒子との混合割合を重量比で99:1とし、30分混合した。

【0039】これを500mlのセパラブルフラスコに入れ、攪拌しながらメタノール含有窒素キャリアガスをフィードして加熱し、300℃の温度で9分処理して三酸化タングステンが添加されたインジウム錫酸化物微粒子を得た。

【0040】上記微粒子20重量%、メチルイソブチルケトン63.3重量%、分散剤16.7重量%、および、充填率63%相当の0.3mmジルコニアビーズをペイントシェーカーで24時間分散した。

【0041】次に、上記分散液67.5重量%、バインダーとしてメチルイソブチルケトンに溶解したアクリル樹脂溶液27.5重量%および硬化剤5重量%からなる塗布液を、パーNo.40、No.24、No.6でそれぞれ100mm×100mm×3mmのソーダライムガラス基板に塗布した後、180℃で30分焼成して日射遮蔽膜aを得た。この日射遮蔽膜aの日射透過率(%)およびヘイズ値(%)を以下の表1に示す。

【0042】そして、この表1から確認されるように、実施例1に係る日射遮蔽膜aの日射透過率およびヘイズ値は、それぞれ67.0%、0.62%であった。

【0043】【実施例2】インジウム錫酸化物微粒子と三酸化タングステン微粒子との混合割合を重量比で98:2とした以外は実施例1と同様にして実施例2に係る日射遮蔽膜bを得た。この日射遮蔽膜bの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0044】そして、この表1から確認されるように、実施例2に係る日射遮蔽膜bの日射透過率およびヘイズ値は、それぞれ68.0%、0.80%であった。

【0045】【実施例3】インジウム錫酸化物微粒子と三酸化タングステン微粒子との混合割合を重量比で96:4とした以外は実施例1と同様にして実施例3に係る日射遮蔽膜cを得た。この日射遮蔽膜cの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0046】そして、この表1から確認されるように、

実施例3に係る日射遮蔽膜cの日射透過率およびヘイズ値は、それぞれ67.1%、0.60%であった。

【0047】【実施例4】インジウム錫酸化物微粒子と三酸化タングステン微粒子との混合割合を重量比で88:12とした以外は実施例1と同様にして実施例4に係る日射遮蔽膜dを得た。この日射遮蔽膜dの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0048】そして、この表1から確認されるように、実施例4に係る日射遮蔽膜dの日射透過率およびヘイズ値は、それぞれ67.0%、0.35%であった。

【0049】【実施例5】インジウム錫酸化物微粒子と三酸化タングステン微粒子との混合割合を重量比で82:18とした以外は実施例1と同様にして実施例5に係る日射遮蔽膜eを得た。この日射遮蔽膜eの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0050】そして、この表1から確認されるように、実施例5に係る日射遮蔽膜eの日射透過率およびヘイズ値は、それぞれ68.9%、0.75%であった。

【0051】【比較例1】三酸化タングステンを添加しない条件で、上記インジウム錫酸化物微粒子を、300℃で9分間加熱処理した場合、日射透過率が70%以上となってしまったため、処理時間を60分とし、それ以外は実施例1と同様にして比較例1に係る日射遮蔽膜fを得た。この日射遮蔽膜fの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0052】そして、この表1から確認されるように、比較例1に係る日射遮蔽膜fの日射透過率およびヘイズ値は、それぞれ66.0%、0.40%であった。

【0053】【比較例2】三酸化タングステンを添加しない条件で、処理時間を180分とし、それ以外は実施例1と同様にして比較例2に係る日射遮蔽膜gを得た。この日射遮蔽膜gの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0054】そして、この表1から確認されるように、比較例2に係る日射遮蔽膜gの日射透過率およびヘイズ値は、それぞれ66.5%、0.46%であった。

【0055】これ等の結果、各実施例に係る日射遮蔽膜と同様の特性を有する日射遮蔽膜を得るためには、処理時間を各実施例の9分間より長い60分間、180分間とする必要があることが確認された。

【0056】【実施例6】処理温度を350℃にした以外は実施例1と同様にして実施例6に係る日射遮蔽膜hを得た。この日射遮蔽膜hの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0057】そして、この表1から確認されるように、実施例6に係る日射遮蔽膜hの日射透過率およびヘイズ値は、それぞれ68.1%、0.35%であった。

【0058】【実施例7】メタノール含有窒素キャリアガスに代えてN₂をキャリアーとした5%H₂ガスを用い、300℃で60分処理した以外は実施例1と同様に

して実施例7に係る日射遮蔽膜iを得た。この日射遮蔽膜iの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0059】そして、この表1から確認されるように、実施例7に係る日射遮蔽膜iの日射透過率およびヘイズ値は、それぞれ66.0%、0.63%であった。

【0060】〔比較例3〕三酸化タングステンを添加しない条件で、上記インジウム錫酸化物微粒子を、300℃で60分間加熱処理した場合、日射透過率が70%以上となってしまうため、処理時間を480分とし、それ以外は実施例7と同様にして比較例3に係る日射遮蔽膜jを得た。この日射遮蔽膜jの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0061】そして、この表1から確認されるように、比較例3に係る日射遮蔽膜jの日射透過率およびヘイズ値は、それぞれ67.1%、0.46%であった。

【0062】この結果、実施例7に係る日射遮蔽膜iと同様の特性を有する日射遮蔽膜を得るためには、処理時間を実施例7の60分間より長い480分間とする必要があることが確認された。

【0063】〔実施例8〕錫含有量10重量%、残留不純物量0.1重量%、平均粒径0.03μmのインジウム錫酸化物微粒子〔住友金属鉱山(株)社製〕と三酸化タングステン微粒子との混合割合を重量比で99:1とし、メタノール含有窒素キャリアガスをフィードして加熱し、300℃で3分処理した以外は実施例1と同様にして実施例8に係る日射遮蔽膜kを得た。この日射遮蔽膜kの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0064】そして、この表1から確認されるように、実施例8に係る日射遮蔽膜kの日射透過率およびヘイズ値は、それぞれ66.7%、0.58%であった。

【0065】〔実施例9〕N₂をキャリアーとした5% H₂ガスを用い、260℃で40分処理した以外は実施

例8と同様にして実施例9に係る日射遮蔽膜lを得た。この日射遮蔽膜lの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0066】そして、この表1から確認されるように、実施例9に係る日射遮蔽膜lの日射透過率およびヘイズ値は、それぞれ69.9%、0.90%であった。

【0067】〔実施例10〕N₂ガスを用い、300℃で10分処理した以外は実施例8と同様にして実施例10に係る日射遮蔽膜mを得た。この日射遮蔽膜mの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0068】そして、この表1から確認されるように、実施例10に係る日射遮蔽膜mの日射透過率およびヘイズ値は、それぞれ69.8%、0.64%であった。

【0069】〔比較例4〕N₂ガスを用いる条件で、錫含有量10重量%、残留不純物量0.7重量%、平均粒径0.03μmのインジウム錫酸化物微粒子〔住友金属鉱山(株)社製〕を300℃で9分間加熱処理した場合、日射透過率が70%以上となってしまうため、処理時間を60分とし、それ以外は実施例1と同様にして比較例4に係る日射遮蔽膜nを得た。この日射遮蔽膜nの日射透過率(%)およびヘイズ値(%)も以下の表1に示す。

【0070】そして、この表1から確認されるように、比較例4に係る日射遮蔽膜nの日射透過率およびヘイズ値は、それぞれ69.6%、0.60%であった。

【0071】この結果、錫含有量10重量%、残留不純物量0.1重量%、平均粒径0.03μmのインジウム錫酸化物微粒子が適用された実施例10に係る日射遮蔽膜mと同様の特性を有する日射遮蔽膜を得るためには、処理時間を実施例10の10分間より長い60分間とする必要があることが確認された。

【0072】

【表1】

	ITO:WO ₃ (重量%)	雰囲気	処理温度 (°C)	処理時間 (分)		可視光透過率 86% 固定	
						日射透過率 (%)	ヘイズ値 (%)
実施例 1	99 : 1	メタノール/N ₂	300	9	膜 a	67.0	0.62
実施例 2	98 : 2	メタノール/N ₂	300	9	膜 b	68.0	0.80
実施例 3	96 : 4	メタノール/N ₂	300	9	膜 c	67.1	0.60
実施例 4	88 : 12	メタノール/N ₂	300	9	膜 d	67.0	0.35
実施例 5	82 : 18	メタノール/N ₂	300	9	膜 e	68.9	0.75
比較例 1	100 : 0	メタノール/N ₂	300	60	膜 f	66.0	0.40
比較例 2	100 : 0	メタノール/N ₂	300	180	膜 g	66.5	0.46
実施例 6	99 : 1	メタノール/N ₂	350	9	膜 h	68.1	0.35
実施例 7	99 : 1	5%H ₂ /N ₂	300	60	膜 i	66.0	0.63
比較例 3	100 : 0	5%H ₂ /N ₂	300	480	膜 j	67.1	0.46
実施例 8	99 : 1	メタノール/N ₂	300	3	膜 k	66.7	0.58
実施例 9	99 : 1	5%H ₂ /N ₂	260	40	膜 l	69.9	0.90
実施例 10	99 : 1	N ₂	300	10	膜 m	69.8	0.64
比較例 4	99 : 1	N ₂	300	60	膜 n	69.6	0.60

【実施例 11】 錫含有量 10 重量%、残留不純物量 0.7 重量%、平均粒径 0.03 μm のインジウム錫酸化物微粒子〔住友金属鉱山（株）社製〕と三酸化レニウム微粒子との混合割合を重量比で 99.5 : 0.5 とし、30 分混合した。

【0073】これを 500 ml のセパラブルフラスコに入れ、攪拌しながらメタノール含有窒素キャリアガスをフィードして加熱し、300℃の温度で 7 分処理して三酸化レニウムが添加されたインジウム錫酸化物微粒子を得た。

【0074】上記微粒子 20 重量%、メチルイソブチルケトン 63.3 重量%、分散剤 16.7 重量%、および、充填率 63% 相当の 0.3 mm ジルコニアビーズをペイントシェーカーで 24 時間分散した。

【0075】次に、上記分散液 67.5 重量%、バインダーとしてメチルイソブチルケトンに溶解したアクリル樹脂溶液 27.5 重量%および硬化剤 5 重量%からなる塗布液を、バー No. 40、No. 24、No. 6 でそれぞれ 100 mm × 100 mm × 3 mm のソーダライムガラス基板に塗布した後、180℃で 30 分焼成して日射遮蔽膜 o を得た。この日射遮蔽膜 o の日射透過率 (%) およびヘイズ値 (%) を以下の表 2 に示す。

【0076】そして、この表 2 から確認されるように、実施例 11 に係る日射遮蔽膜 o の日射透過率およびヘイズ値は、それぞれ 67.7%、0.30% であった。

【0077】【実施例 12】インジウム錫酸化物微粒子と三酸化レニウム微粒子との混合割合を重量比で 99.9 : 0.1 とした以外は実施例 11 と同様にして実施例 12 に係る日射遮蔽膜 p を得た。この日射遮蔽膜 p の日射透過率 (%) およびヘイズ値 (%) も以下の表 2 に示す。

【0078】そして、この表 2 から確認されるように、

実施例 12 に係る日射遮蔽膜 p の日射透過率およびヘイズ値は、それぞれ 67.5%、0.30% であった。

【0079】【実施例 13】インジウム錫酸化物微粒子と三酸化レニウム微粒子との混合割合を重量比で 99.2 : 0.8 とした以外は実施例 11 と同様にして実施例 13 に係る日射遮蔽膜 q を得た。この日射遮蔽膜 q の日射透過率 (%) およびヘイズ値 (%) も以下の表 2 に示す。

【0080】そして、この表 2 から確認されるように、実施例 13 に係る日射遮蔽膜 q の日射透過率およびヘイズ値は、それぞれ 68.5%、0.29% であった。

【0081】【比較例 5】三酸化レニウムを添加しない条件で、上記インジウム錫酸化物微粒子を、300℃で 7 分間加熱処理した場合、日射透過率が 70% 以上となってしまうため、処理時間を 60 分とし、それ以外は実施例 11 と同様にして比較例 5 に係る日射遮蔽膜 r を得た。この日射遮蔽膜 r の日射透過率 (%) およびヘイズ値 (%) も以下の表 2 に示す。

【0082】そして、この表 2 から確認されるように、比較例 5 に係る日射遮蔽膜 r の日射透過率およびヘイズ値は、それぞれ 66.0%、0.40% であった。

【0083】【比較例 6】三酸化レニウムを添加しない条件で、処理時間を 180 分とし、それ以外は実施例 11 と同様にして比較例 6 に係る日射遮蔽膜 s を得た。この日射遮蔽膜 s の日射透過率 (%) およびヘイズ値 (%) も以下の表 2 に示す。

【0084】そして、この表 2 から確認されるように、比較例 6 に係る日射遮蔽膜 s の日射透過率およびヘイズ値は、それぞれ 66.5%、0.46% であった。

【0085】これ等の結果、実施例 11 ~ 13 に係る日射遮蔽膜と同様の特性を有する日射遮蔽膜を得るためには、処理時間を各実施例の 7 分間より長い 60 分間、1

80分間とする必要があることが確認された。

【0086】【実施例14】処理温度を350℃にした以外は実施例11と同様にして実施例14に係る日射遮蔽膜tを得た。この日射遮蔽膜tの日射透過率(%)およびヘイズ値(%)も以下の表2に示す。

【0087】そして、この表2から確認されるように、実施例14に係る日射遮蔽膜tの日射透過率およびヘイズ値は、それぞれ68.6%、0.39%であった。

【0088】【実施例15】メタノール含有窒素キャリアガスに代えてN₂をキャリアーとした5% H₂ガスを用い、300℃で60分処理した以外は実施例11と同様にして実施例15に係る日射遮蔽膜uを得た。この日射遮蔽膜uの日射透過率(%)およびヘイズ値(%)も以下の表2に示す。

【0089】そして、この表2から確認されるように、実施例15に係る日射遮蔽膜uの日射透過率およびヘイズ値は、それぞれ66.8%、0.29%であった。

【0090】【比較例7】三酸化レニウムを添加しない条件で、上記インジウム錫酸化物微粒子を、300℃で60分間加熱処理した場合、日射透過率が70%以上となってしまうため、処理時間を480分とし、それ以外は実施例15と同様にして比較例7に係る日射遮蔽膜vを得た。この日射遮蔽膜vの日射透過率(%)およびヘイズ値(%)も以下の表2に示す。

【0091】そして、この表2から確認されるように、比較例7に係る日射遮蔽膜vの日射透過率およびヘイズ値は、それぞれ67.1%、0.46%であった。

【0092】この結果、実施例15に係る日射遮蔽膜uと同様の特性を有する日射遮蔽膜を得るためには、処理時間を実施例15の60分間より長い480分間とする必要があることが確認された。

【0093】【実施例16】錫含有量10重量%、残留不純物量0.1重量%、平均粒径0.03μmのインジウム錫酸化物微粒子〔住友金属鉱山(株)社製〕と三酸化レニウム微粒子との混合割合を重量比で99.5:0.5とし、メタノール含有窒素キャリアガスをフィー

ドして加熱し、270℃で40分処理した以外は実施例11と同様にして実施例16に係る日射遮蔽膜wを得た。この日射遮蔽膜wの日射透過率(%)およびヘイズ値(%)も以下の表2に示す。

【0094】そして、この表2から確認されるように、実施例16に係る日射遮蔽膜wの日射透過率およびヘイズ値は、それぞれ69.5%、0.42%であった。

【0095】【実施例17】N₂ガスを用い、300℃で10分処理した以外は実施例16と同様にして実施例17に係る日射遮蔽膜xを得た。この日射遮蔽膜xの日射透過率(%)およびヘイズ値(%)も以下の表2に示す。

【0096】そして、この表2から確認されるように、実施例17に係る日射遮蔽膜xの日射透過率およびヘイズ値は、それぞれ69.9%、0.35%であった。

【0097】【比較例8】N₂ガスを用いる条件で、錫含有量10重量%、残留不純物量0.7重量%、平均粒径0.03μmのインジウム錫酸化物微粒子〔住友金属鉱山(株)社製〕を300℃で10分間加熱処理した場合、日射透過率が70%以上となってしまうため、処理時間を60分とし、それ以外は実施例11と同様にして比較例8に係る日射遮蔽膜yを得た。この日射遮蔽膜yの日射透過率(%)およびヘイズ値(%)も以下の表2に示す。

【0098】そして、この表2から確認されるように、比較例8に係る日射遮蔽膜yの日射透過率およびヘイズ値は、それぞれ69.6%、0.33%であった。

【0099】この結果、錫含有量10重量%、残留不純物量0.1重量%、平均粒径0.03μmのインジウム錫酸化物微粒子が適用された実施例17に係る日射遮蔽膜xと同様の特性を有する日射遮蔽膜を得るためには、処理時間を実施例17の10分間より長い60分間とする必要があることが確認された。

【0100】

【表2】

	ITO:ReO ₃ (重量%)	雰囲気	処理温度 (°C)	処理時間 (分)		可視光透過率 86% 固定	
						日射透過率 (%)	ヘイズ値 (%)
実施例11	99.5 : 0.5	Ar/N ₂	300	7	膜 o	67.7	0.30
実施例12	99.9 : 0.1	Ar/N ₂	300	7	膜 p	67.5	0.30
実施例13	99.2 : 0.8	Ar/N ₂	300	7	膜 q	68.5	0.29
比較例5	100 : 0	Ar/N ₂	300	60	膜 r	66.0	0.40
比較例6	100 : 0	Ar/N ₂	300	180	膜 s	66.5	0.46
実施例14	99.5 : 0.5	Ar/N ₂	350	7	膜 t	68.6	0.39
実施例15	99.5 : 0.5	5%H ₂ /N ₂	300	60	膜 u	66.8	0.29
比較例7	100 : 0	5%H ₂ /N ₂	300	480	膜 v	67.1	0.46
実施例16	99.5 : 0.5	Ar/N ₂	270	40	膜 w	69.5	0.42
実施例17	99.5 : 0.5	N ₂	300	10	膜 x	69.9	0.35
比較例8	99.5 : 0.5	N ₂	300	60	膜 y	69.6	0.33

【0101】

【発明の効果】請求項1～4記載の発明に係る日射遮蔽膜形成用微粒子の製造方法によれば、加熱処理時に、
 20 錫含有酸化インジウム微粒子に添加されたタングステン酸化物微粒子またはレニウム酸化物微粒子の触媒作用により、可視光透過率80%以上のときの日射透過率が70%未満でしかもヘイズ値が1%未満である日射遮蔽

膜を形成可能な日射遮蔽膜形成用微粒子を従来よりも短時間で製造できる効果を有しており、また、請求項5記載の発明に係る日射遮蔽膜形成用塗布液によれば、可視光透過率80%以上のときの日射透過率が70%未満でしかもヘイズ値が1%未満である日射遮蔽膜を形成できる効果を有している。

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